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A SECOND DIGEST OF INFORMATION ON ALLETHRIN AND RELATED COMPOUNDS

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In 1952 the Bureau of Entomology and Plant Quarantine issued a digest (E-846) of the information on allethrin available up to that time. During the last 3 years our knowledge of allethrin has been greatly extended, and it is the purpose of this digest to summarize this additional information, and also to present information on the closely related insecticides furethrin and cyclethrin.

ANALYSIS

Methods of assaying technical allethrin have been studied by members of the Association of Official Agricultural Chemists (AOAC) and the Chemical Specialties Manufacturers' Association (CSMA).

At the recommendation of Konecky (55), associate referee on methods of analysis of allethrin, the AOAC at its 1952 meeting approved a continuation of studies on the hydrogenation and ethylenediamine methods of analysis for technical allethrin.

In 1953 the CSMA chemical analysis committee reported acceptance of the ethylenediamine method for allethrin assay (Hill 43). As described by Hogsett et al. (47), allethrin is reacted with ethylenediamine to form the amine salt of chrysanthemumic acid, which is titrated with standard sodium methylate in pyridine solution. Chrysanthemumic acid, anhydride, or acid chloride, if present in the sample, is determined independently, and corrections are applied to obtain the true allethrin content. This method provides a specific and accurate means of evaluating allethrin and related compounds as produced. Preliminary investigations indicate that it may also be useful for the determination of allethrin in insecticide formulations.

A method for the estimation of micro quantities of pyrethroids has been described by Schreiber and McClellan (96). It is a modification of the AOAC method for pyrethrin I. A sample of allethrin or pyrethrin I containing about 10 to 100 micrograms of chrysanthemumic acid in petroleum ether is hydrolyzed with 0.1 N ethanolic sodium hydroxide, the alcohol boiled off, barium chloride solution added, filtered, the filtrate strongly acidified with 20-percent sulfuric acid and extracted with petroleum ether, and the allethrin determined colorimetrically with a modified Deniges reagent.

The reaction of sodium sulfide with pyrethrins, allethrin, and furethrin is used by Cueto and Dale (15) for their determination. The color is developed in an alcoholic solution, and readings are made on a colorimeter at 540 mu. Beer's law is followed in the range of 0.5 to 10 mg.

The Japanese workers Oiwa and associates (82, 83, 84) and Katuda et al. (52) have investigated the polarographic determination of allethrin and pyrethrins, and conclude that the method gives reliable results. They used crystalline allethrin as a standard in this work.

Green and Schechter (40) have described a procedure for the determination of allethrin based on its conversion to the dinitrophenylhydrazone derivative, chromatography of the derivative on silicic acid, and gravimetric or colorimetric determination of the main band. What appears to be a somewhat similar method has been investigated by Moore (73) working in the Pest Infestation Research Board of Great Britain (39). Using 2,4-dinitrophenylhydrazine it has been possible to estimate the allethrin content of commercial samples by either gravimetric or spectrophotometric means, but further trials are necessary before the value of the method can be fully established. Crystalline allethrin, first described by Schechter et al. (item 160 in E-846) in 1951, was used as a standard and when assayed by this method showed a purity of 99.7 percent.

A spectrophotometric assay of allethrolone has been proposed by Freeman (25). This consists in measuring the absorbency of the compound in ethyl alcohol at 231 mu. Analyses of several samples of this pure material show the accuracy of the procedure to be within $\pm$0.5 percent, with a standard deviation of 0.24 percent for a single determination. An average difference of 0.26 percent between duplicates was obtained in routine analyses of more than 50 allethrolone samples.

Freeman (26), by the combined techniques of partition chromatography and infrared spectrometry, isolated and identified chrysanthemumic acid anhydride in several commercial allethrin samples. In addition, he obtained a high-purity allethrin assaying over 98 percent, and the partial separation of cis and trans allethrins on a chromatographic column was quantitatively followed.

Winteringham (121), working in the Pest Infestation Research Board of Great Britain (38), described a method of separating the pyrethrins and their acid and alcohol products of hydrolysis by reversed-phase paper chromatography. Allethrin also can be separated from its hydrolysis products by this method. The separated zones on the paper strips are developed by treatment with potassium permanganate and subsequent application of benzidine in dilute acetic acid, which produces a blue color where manganese dioxide has been formed in the presence of the unsaturated compounds of the pyrethrin type. Using this method Acree and Babers (4) separated dl-cis from dl-trans labeled and unlabeled chrysanthemumic acids by paper chromatography.

Allethrin interferes in the colorimetric method for pyrethrins devised by Levy and Estrada (61). This method permits the determination of total pyrethrins down to a concentration of about 0.04 mg. per milliliter, based on the measurement of a red color developed by pyrethrum extracts upon addition of sulfur solutions in alcoholic potassium hydroxide and in carbon tetrachloride. Kerosene, synergists, or DDT do not affect the results. The method has been successfully applied for the rapid determination of total pyrethrins in pyrethrum

flowers and in commercial oil-base insecticides. Allethrolone, 1 mg., gives a Klett-Summerson reading of 40 as compared with 290 for pyrethrins, when a 560 mu. filter is employed.

Allethrin interferes in the colorimetric method of piperonyl butoxide devised by Jones et al. (51). A clear blue color of good stability is obtained when a solution of piperonyl butoxide in purified kerosene is heated with a solution of tannic acid in a mixture of phosphoric and glacial acetic acids. Pyrethrins reduce the intensity of the blue color, and in preliminary work allethrin has shown about the same degree of interference.

BIOASSAY OF ALLETHRIN

A method of bioassay of pyrethrins that is applicable to allethrin has been developed by the Pest Infestation Research Board of Great Britain (38). This method is based on the observation that flour beetles lose weight rapidly on being treated with pyrethrins, the weight lost in a given time being related to the dosage. The procedure for bioassay is, briefly, as follows: Whatman No. 544 filter papers are sprayed with pyrethrins in kerosene at a fixed level of deposit. Papers of one series are treated with dilutions of a standard concentrate of known pyrethrins content, and those of another series with dilutions of the preparation of unknown pyrethrins content. Beetles in batches of 100, each weighed to the nearest 0.1 mg., are exposed on the papers at 25° C. and 70 percent relative humidity for 3 hours and then weighed again. Control batches are similarly exposed on untreated papers. Under the conditions of exposure, the maximum weight loss, adjusted for that in the controls, is about 7 percent, however high the pyrethrins concentration. By statistical analysis these losses in weight can be used to estimate the potency of the test preparation relative to the standard, whence its pyrethrins content can also be estimated.

CHEMISTRY OF ALLETHRIN AND RELATED COMPOUNDS

Inouye et al. (50) reported the synthesis of chrysanthemum dicarboxylic acid, m.p. 180-180.5° C., after recrystallization from chloroform and then water. This is considered to be one of the four racemic stereoisomers possible for the synthetic chrysanthemum dicarboxylic acid.

Blackith (7) found allethrin to be more stable to ultraviolet photolysis than the natural pyrethrins. As it is less well protected by benzeneazo-beta-naphthol, the two insecticides have a similar stability in protected films.

LaForge and Green (56) reported the synthesis of d-cinerolone, cinerin I, and its optical isomers. The synthesis of cinerin I was completed by the resolution of synthetic 2-(cis-2-butenyl)-4-hydroxy-3-methylcyclopenten-1-one into its d and l isomeric forms, the previous steps having already been accomplished.

LaForge et al. (57) reported the resolution of dl-allethrolone and the synthesis of the four optical isomers of trans-allethrin. dl-Allethrolone was resolved into its d and l forms by a procedure involving esterification with d-trans-chrysanthemumic acid (via the acid chloride), formation and fractional crystallization of the semicarbazones of the mixed diasteroisomeric esters, methanolysis of the separated ester semicarbazones, and cleavage of the optically active d-allethrolone from its semicarbazone. Each of these optically active allethrolones was esterified with d- and l-trans-chrysanthemumic acids to give four of the eight possible optically active isomers of allethrin. A crystalline isomer of allethrin previously reported was determined to be a racemic compound of d-allethrolone l-trans-crysanthemumate and l-allethrolone d-trans-chrysanthemumate.

Elliott (21) reviewed the synthetic work leading to the commercial preparation of allethrin and described the effect of various changes in the molecule on insecticidal activity. The biological action of allethrin appears to be similar to that of the natural pyrethrins, and is associated with the particular stereochemical conformation in which the various parts of the molecule are held with respect to each other and with the chemical and physical properties of the groups so positioned.

RADIOACTIVE ALLETHRIN

Acree et al. (5) announced the synthesis of radioactive allethrin starting with 2-C^{14}-glycine and following the procedure already established for the preparation of unlabeled allethrin. After purification by chromatography the radioactive allethrin appeared to be approximately 98 percent pure. This material will be used in a study of the penetration and metabolic fate of toxic esters of chrysanthemumic acid in connection with their toxicological and resistance phenomena in the house fly and cockroaches.

The Pest Infestation Research Board of Great Britain (38) reported the synthesis of radioactive allethrin starting with acetone in which carbons 1 and 3 were C^{14}. This acetone was oxidized to pyruvaldehyde with selenium dioxide and the synthesis continued as described by Schechter et al. in 1949 (item 154 in E-846). The allethrin obtained in this way contains two labeled carbon atoms, both in the allethrolone portion of the molecule, whereas Acree's product contains one labeled carbon atom in the chrysanthemumic acid portion.

FURETHRIN

A method of making furethrin by reacting 2-furfuryl-3-methyl-4-hydroxy-2-cyclopenten-1-one with chrysanthemum monocarbonyl chloride was patented in Japan by Matsui (69). The product has a boiling point of 155-160° C. at 0.01 mm. and a refractive index (n_D^{20}) of 1.5120.

Spray tests comparing furethrin, allethrin, and pyrethrins against the house fly were reported by Fales *et al.* (23). The dosage was 55.56 ml. per 1,000 cubic feet with concentrations of 1 and 2 mg. per milliliter. Allethrin was below furethrin and pyrethrins in 5-minute knockdown but was superior in mortality.

CYCLETHRIN

Cyclethrin was first announced at the May 1954 meeting of the Chemical Specialties Manufacturers' Association (Haynes *et al.* 42). A reporter of this announcement (2) surmised that cyclethrin can be competitively priced with allethrin ($32 per pound, 100-percent basis) and that the manufacturer who can make 500,000 pounds of allethrin per year could easily alter production to make this newer insecticide.

According to Haynes *et al.* (42), cyclethrin resembles allethrin except for a cyclopentenyl radical in place of the allyl radical. Its chemical name is 3-(2-cyclopentenyl)-2-methyl-4-oxo-2-cyclopentenyl chrysanthemum monocarboxylate. It is a viscous straw-colored liquid readily soluble in kerosene and the Freons. Its mammalian toxicity is no greater than that of allethrin and by certain routes it is considerably less. In Peet-Grady tests against house flies cyclethrin provided slightly less knockdown at 3 minutes than allethrin or pyrethrins. There was no difference between the three materials in 10-minute knockdown or in kill of down flies in 24 hours. Cyclethrin is synergized to a greater degree than allethrin with sulfoxide, piperonyl butoxide, *n*-propyl isome, and synergist 6266. Approximately equal results were obtained with sprays containing 200 mg. of piperonyl butoxide or sulfoxide in combination with 25 mg. of pyrethrins, 42 to 50 mg. of cyclethrin, or 75 to 100 mg. of allethrin. These concentrations are on the basis of 100 ml. of refined petroleum distillate.

In tests by the Campbell turntable method Gersdorff and Piquett (33) found that cyclethrin was 0.6 as toxic as allethrin and 1.5 as toxic as pyrethrins. Cyclethrin was synergized more strongly by either piperonyl butoxide or sulfoxide than was allethrin but to a lesser degree than pyrethrins. The knockdown results appeared to parallel those for mortality. In simple sprays cyclethrin was a little less effective than allethrin, but mixtures containing cyclethrin were slightly more effective than those containing allethrin.

The acute and subacute toxicity of cyclethrin to mammals has been studied by Carpenter et al. (12). They report its LD-50 for rats to be 1.4 to 2.8 grams per kilogram. Its toxic action is of the same nature and range as pyrethrins.

CRYSTALLINE ALLETHRIN ISOMER

The crystalline allethrin isomer described by Schechter et al. (item 160 in E-846) has been studied by several workers of the CSMA (see Starr 99, 100, 101) as a possible standard material for bioassay purposes. This possible use was noted in the Annual Report of the Bureau of Entomology and Plant Quarantine for 1952 (111).

Storage tests at room temperature and 6° C. have shown no evidence of chemical breakdown of the crystalline isomer as determined by bioassay tests on house flies (Kido 54).

Nagasawa (77, 78, 79) made use of this crystalline isomer of allethrin as a standard in the biological assay of insecticides and in comparing the knock-down value of pyrethrins I and II.

EFFECT OF STRUCTURE OF ALLETHRIN-LIKE ESTERS ON THEIR CONTACT TOXICITY

Mitlin et al. (72) reported tests with some derivatives of chrysanthemumic acid against house flies. Esters of this acid with alcohols, and phenols, and amides showed little toxicity at the concentrations tested. All were less than 0.06 as effective as pyrethrins, most of them less than 0.03. The ester of a mixture of cis- and trans-dl-chrysanthemumic acids with furfuryl alcohol gave knockdown of 86 percent in 25 minutes but a mortality of only 6 percent in 24 hours.

Chen and Barthel (14) synthesized five new pyrethrin-type esters. The esters prepared from phenyl- and benzyl-substituted methylcyclopentenolones and dl-chrysanthemumic acid were of the same order of toxicity as natural pyrethrins. Substitution of methoxy or methylenedioxy groups in the aryl nucleus greatly decreased the toxicity.

The effect on insecticidal activity of altering the structure of the acid parts of pyrethrin-like esters was studied at the Rothamsted Experimental Station (88) by a measured-drop technique with Dysdercus fasciatus, Phaedon cochleariae, and Tenebrio molitor as the test insects. The esters of d-trans and d-cis forms of chrysanthemumic acid were found to be more toxic than the l-trans and the l-cis forms.

LaForge and Green (56) reported the ester made by combining l-cis-cinerolone and d-trans-chrysanthemumic acid to be more toxic to house flies than the other possible combinations of cinerolones and chrysanthemumic acids.

Campbell and Mitchell (11) found the allethrolone ester of the d-trans-chrysanthemumic acid to be nearly twice as toxic to house flies as the natural mixture of pyrethrins. The knockdown behavior was quite different from that due to pyrethrum. At first it was slower, though substantially complete in 3 minutes, but after 6 minutes the flies became highly activated; although their legs remained paralyzed, they appeared to recover the normal use of their wings. The knockdown effect, though superior to that of most other synthetic insecticides, is definitely poorer than that of pyrethrum.

Gersdorff and Mitlin (27) in tests with the turntable method found the methyl analog of allethrin to be 0.12 as toxic to house flies as allethrin and 0.40 as toxic as pyrethrins, and the ethyl analog 0.26 as toxic as allethrin and 0.94 as toxic as pyrethrins. Knockdown was complete for both analogs at the concentrations used.

Gersdorff and Mitlin (28) evaluated the relative toxicity to house flies of the four trans stereoisomers of allethrin in comparison by the turntable method. The l-allethrolone d-trans-chrysanthemumic acid ester and the d-l, l-l, and d-d esters were, respectively, 0.58, 0.14, 0.022, and 3.4 as toxic as allethrin. With the same acid component the change from the l to the d form of the allethrolone component was accompanied by a 6-fold increase in toxicity. With the same allethrolone component the change from the l to the d form of the acid component was accompanied by a 25-fold increase in toxicity. The decreasing order of effectiveness in both knockdown action and mortality was the d-allethrolone d-chrysanthemumic acid ester, the l-d ester, the d-l ester, and the l-l ester. The decrease was greater for knockdown, especially in the last two esters.

Gersdorff and Mitlin (29) found that the phenyl, benzyl, o-methoxybenzyl, p-methoxybenzyl, and 3,4-methylenedioxybenzyl analogs of allethrin were, respectively, 34, 18, 7, 2, and 6 percent as toxic to house flies as allethrin.

MANUFACTURE

The 18 steps used by the Baltimore plant of the United States Industrial Chemicals Company in making allethrin have been described by Sanders and Taff (93). This plant handles close to a million pounds of chemicals a month. Over 35 raw materials are used, in addition to about 20 intermediates, byproducts, and solvents (Anonymous 1). On September 1, 1954, it was sold to the Food Machinery and Chemical Corporation, which is continuing the pesticide operations as its Fairfield Chemical Division (Anonymous 3).

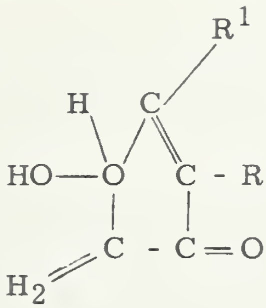
According to the Production and Marketing Administration (114), about 60,000 pounds of allethrin were produced during 1952, the first full year of commercial production. This quantity is roughly equivalent in insecticidal value to two-thirds of the pyrethrum imported during the year.

According to a report by the Commodity Stabilization Service (113) issued in April 1954, allethrin was in adequate production to meet any conceivable demands. It is used chiefly in pressurized aerosol dispensers and in oil-base insecticides of the household type.

PATENTS

A crystalline isomer of allethrin which is an ester of dl-trans-chrysanthemumic acid is obtained by cooling a solution of technical allethrin in isooctane or other inert liquid hydrocarbon solvent. This cyrstalline isomer, known as alpha-dl-trans allethrin, melts at 50-51° C. when purified. A patent covering this process was granted Schechter and LaForge (94) in 1952.

In 1953 Schechter and LaForge (95) were granted a patent for a method of preparing a cyclopentenolone of the formula



which comprises treating a hydroxydiketone of the formula R'-CO-CHOH-CH_2-CO-CH_2-R with an alkaline cyclizing agent, R' being taken from the group consisting of alkyl, alkenyl, and aryl radicals, and R from the group consisting of alkyl, alkenyl, substituted alkenyl, aryl, aralkyl, cycloalkyl, and cycloalkenyl radicals. When R is allyl (-CH_2CH=CH_2) and R' is methyl, the compound is allethrolone, the alcohol portion of the ester allethrin.

SPECIFICATION FOR ALLETHRIN

At the December 1953 meeting of the CSMA Insecticide Chemical Analysis Committee, Hill (44) presented a letter from M. S. Schechter advocating the lowering of the total free-acidity limit for technical allethrin from 8 percent to a figure more in line with current production batches, which seemed to be running not over 3 percent. Schechter suggested raising the minimum purity of technical allethrin from 75 percent to some higher figure.

SYNERGISTS FOR ALLETHRIN

Gersdorff et al. (31) reported that certain N-substituted piperonylamides synergized allethrin in oil space sprays when tested against the house fly. Unsubstituted piperonylamide was the only compound of 23 tested not affecting the toxicity when applied jointly with allethrin. The most effective synergists were N-o-tolyl, N,N-diethyl, N-propyl, and N-(o-bromophenyl) piperonylamides. Twelve of these sprays gave house fly mortalities three or more times greater than expected on the basis of equivanents.--U. S. Bureau of Entomology and Plant Quarantine (112).

Mitlin et al. (71) reported similar studies with a number of N-substituted compounds. The greatest effect was to raise toxicity to about twice that expected for allethrin alone. This effect was obtained with N-amyl-2,4-dinitroaniline, N-amyl-o-chlorobenzamide, and N-sec-amyl-o-chlorobenzamide.

In studies with sulfoxide as a synergist for pyrethrum and allethrin in sprays and aerosols, Fales et al. (22) found it to rank with piperonyl butoxide. It was less effective with allethrin than with pyrethrum. In sprays containing allethrin and DDT, sulfoxide and piperonyl butoxide acted similarly.

Incho and Ault (49) tested the furfuryl, thenyl, and benzyl analogs of allethrin on house flies to determine their effectiveness in oil-base sprays when used alone and with piperonyl butoxide and seven of its analogs. When tested alone the allethrin analogs were less effective than allethrin alone. However, in combination with piperonyl butoxide and six of its analogs the furfuryl and thenyl analogs were generally equal to or more effective than allethrin. The benzyl analog showed the least activity when tested alone or with the synergists.

Turner (108) reported the results of tests of four synergists for allethrin against the milkweed bug. Piperonyl butoxide, piperonyl cyclonene, and sulfoxide showed no evidence of synergism. There was some increased toxicity when MGK-264 was added, but far less than when this synergist was used with pyrethrum.

Matsubara (67) tested the synergistic value of piperonyl butoxide and egonol with allethrin against larvae of *Culex pipiens* var. *pallens* Coq. Egonol is obtained from the unsaponifiable fraction of egoseed oil (*Styrax japonicum*) and contains a methylenedioxyphenyl grouping. Its degree of synergism for allethrin was 0.761 that of piperonyl butoxide in allethrin mixture, but less in pyrethrin mixtures. From bioassays with these larvae Matsubara (68) observed that piperonyl butoxide was more effective as a synergist for pyrethrins than for allethrin. The difference did not appear to be correlated with the inhibition of the enzymatic detoxification of pyrethroids.

Nagasawa and Nishimura (80) tested MGK-264, *n*-propyl isome, sulfoxide, piperonyl cyclonene, and piperonyl butoxide as synergists for pyrethrins and allethrin in dust form, with the house fly as the test insect. In dusts containing 0.5 percent of synergist and 0.05 percent of toxicant all showed synergism.

Gersdorff *et al.* (32) studied the effect of sulfone at 5 to 1 in allethrin and pyrethrins sprays by the turntable method. Sulfone synergized both insecticides, pyrethrins much more powerfully than allethrin.

Gersdorff *et al.* (30) also found that sesamol and a sterol caused no synergistic effect with pyrethrins, and that sesamolin was much more effective than sesamin. Both sesamin and sesamolin slightly synergized allethrin.

Tsao *et al.* (107) reported that in topical application tests a 1:1 mixture of allethrin and chlorinated terphenyl was 1.3 times as toxic as allethrin alone to the house fly. Chlorinated terphenyl was also found to extend the effective period of allethrin residues.

Turner (109) in studies on the large milkweed bug found no evidence of synergism between nicotine and allethrin.

Eddy *et al.* (19) tested 203 compounds as synergists with allethrin against the body louse. The materials were evaluated as cloth impregnants and in pyrophyllite powders. On the basis of minimum lethal concentration 11 materials proved more efficient than the standard, sulfoxide. Some of them increased the toxicity of allethrin from 10 to 20 times. On a residue basis the following materials were about equal to or slightly more effective than sulfoxide: 1,2-methylenedioxy-4-[2-(octysulfonyl)propyl]benzene, dibutyl piperonylidene ester of malonic acid, and the following esters of chrysanthemumic acid: *alpha*-allylpiperonyl, *alpha*-amylpiperonyl, *alpha*-butylpiperonyl, *alpha*-*tert*-butylpiperonyl, *alpha*-ethylpiperonyl, *alpha*-(2-methylallyl)piperonyl, and 4-(3,4-methylenedioxyphenyl)-*sec*-butyl.

Hopkins and Hoffman (48) found the *alpha*-allyl-, *alpha*-butyl-, *alpha*-ethyl-, *alpha*-(2-methylalkyl)-, and *alpha*-propyl-piperonyl esters of chrysanthemumic acid to increase the initial and residual toxicities of Dilan to DDT-resistant house flies. However, they lost their effectiveness after 7 to 28 days whereas piperonyl butoxide was effective after 42 days.

MIXTURES OF ALLETHRIN AND OTHER INSECTICIDES

Kent *et al.* (53) found that 500 mg. of Strobane per 100 ml. of deodorized petroleum hydrocarbon caused only 9 percent knockdown of house flies in 10 minutes, but that when 45 mg. of allethrin and 225 mg. of piperonyl butoxide were added the knockdown was increased to 86 percent.

EFFECT OF ALLETHRIN ON WHEAT GERMINATION

Wilbur (119) reported tests on the effect of four protectant formulations on the germination of wheat seed. Two of these formulations contained pyrethrins and piperonyl butoxide, one allethrin and piperonyl butoxide, and one pyrethrins and allethrin plus the synergist. No single factor or combination of factors--including variety, moisture content, length of exposure, temperature, protectant formulation, or rate of application--affected the wheat germination in measurable amounts.

PHARMACOLOGY OF ALLETHRIN

Woodward et al. (122) reported that unanesthetized rabbits given 5 mg. of allethrin per kilogram intravenously exhibited muscular twitching, occasional convulsions, and increased sensitivity to stimuli. These symptoms lasted for 1 to 2 hours and were blocked by ether and chloroform, essentially unaffected by atropine, and increased by physostigmine and picrotoxin. Injection of allethrin in phenobarbital-anesthetized dogs and rabbits caused little change in blood pressure but stimulated respiration. Normal rhythm of an isolated rabbit intestine was reversibly inhibited by 8 micrograms of allethrin per milliliter of bathing fluid. During inhibition the intestine was insensitive to nicotine and acetylcholine, but reacted to barium chloride. The response of an isolated rat diaphragm to standard phrenic-nerve stimuli was first increased and then reversibly blocked by 10 micrograms of allethrin per milliliter of bathing fluid. A spontaneously contracting guinea pig uterus was variably affected, both stimulation and depression being observed.

In studies on the subacute and chronic toxicity of pesticides to the rat, reported by Lehman (59) of the Food and Drug Administration, the lowest level of pyrethrins in the diet causing gross effects was 5,000 p.p.m., and of allethrin 10,000 p.p.m.

Lehman (60) stated that allethrin resembles the pyrethrins in toxicity to mammals. Although the rather high intravenous toxicity of the pyrethrins should reflect a high inhalation hazard, this is unlikely in light of its rapid detoxification as shown by the low chronic toxicity.

The Food and Drug Administration (115) on October 20, 1954, published tolerances for poisonous or deleterious residues in or on fresh fruits and vegetables based on hearings held in 1950. It is stated that there is no record basis for establishing a tolerance for allethrin.

INSECTICIDAL VALUE OF ALLETHRIN

The comparative toxicities of allethrin and pyrethrins to several species of insects have been determined by Busvine and Nash (10). Allethrin was generally less effective initially than natural pyrethrins, the ratios of their potencies being *Cimex* 0.17, *Rhodnius* 0.12, *Pediculus* 0.24, *Xenopsylla* 0.17, *Aedes* 0.38, *Musca* 0.72, and *Ornithodoros* 0.13. Allethrin was the most effective against *Musca*. However, allethrin was more persistent in its residual toxicity.

Shawarby (97) determined the median lethal concentrations of several persistent insecticides against fleas and lice. Against the oriental rat flea the toxicities were in the following descending order: gamma BHC, dieldrin, aldrin, chlordane, DDT, pyrethrins, allethrin, and toxaphene. Against lice the order of toxicity was: dieldrin, gamma BHC, aldrin, chlordane, pyrethrins, allethrin, and DDT or toxaphene.

Since the summer of 1952 reports of tests of allethrin against 47 species of insects--representing 28 genera, 15 families, and 8 orders--have been published. The results of these tests are summarized below.

Orthoptera: Blattidae

Blattella germanica (L.), German cockroach

In tests against three strains of cockroaches, one normal, one resistant to DDT, and the other to chlordane, allethrin synergized with MGK-264 was more toxic than DDT and chlordane to all strains and more toxic than dieldrin to the chlordane-resistant strain, but somewhat less toxic than Diazinon to all strains.--Fisk and Isert (24).

Two low-cost aerosol formulations containing 0.1 percent of allethrin, although acceptable against house flies, were found to be appreciably below the Official Test Aerosol in mortality of German cockroaches.--Starr *et al.* (102).

By the topical-application method allethrin was found to be 0.12 as toxic as pyrethrins to both susceptible and resistant cockroaches.--Mitlin and Babers (70).

Periplaneta americana (L.), American cockroach

At a concentration of 10^{-3}M pyrethrins and allethrin completely inhibited cytochrome oxidase obtained from the coxal muscle of the American cockroach.--Morrison and Brown (76).

Allethrin was 0.55 as toxic as pyrethrins to last-instar nymphs of this cockroach.--Mitlin and Babers (70).

Homoptera: Aphididae

Aphis fabae Scop., bean aphid

In field trials in England, sprays containing allethrin (0.05 percent (w/v) gave moderate control of the bean aphid on field beans. -- Way et al. (118).

In other tests allethrin was ineffective.--Glynne et al (37).

Brevicoryne brassicae (L.), cabbage aphid

A pyrophyllite dust containing 0.23 percent of allethrin was ineffective.--Dills and Odland (16).

Hemiptera: Cimicidae

Cimex lectularius L., bed bug

Pyrethrins proved 5.3 times as toxic as allethrin. Piperonyl butoxide was a more powerful synergist than isobutyl undecyleneamide (IN 930), increasing the potency of allethrin three times as compared with twice for IN 930.--Nash (81).

Hemiptera: Pyrrhocoridae

Dysdercus fasciatus Sign.

In tests on Dysdercus eggs of different ages, resistance to allethrin dropped very slightly from the first to the fourth day and then increased rapidly to the eighth day.--Salkeld and Potter (91).

Anoplura: Pediculidae

Pediculus humanus humanus L., body louse

Susceptible body lice from an infested man in London and DDT-resistant lice from the Insect Control Section of the Ministry of Public Health, Cairo, were used for comparative tests of insecticides. The resistant lice were nine times as resistant as were the susceptible lice to DDT and 1.3 times as resistant to gamma BHC. Several other insecticides were then tested against the new DDT-resistant strain. Batches of lice were exposed for 18 hours at 30° C. on filter papers impregnated with oil solutions of different concentrations at the rate of 3 mg. per square centimeter. The median lethal concentration of allethrin was 0.74, and of pyrethrins 0.14.--Busvine (9).

Coleoptera: Chrysomelidae

Phaedon cochleariae F., mustard beetle

The pyrethrins were separated by displacement chromatography, and the biological activity of four of the fractions was tested by topical application in acetone. The LD-50's of these fractions and also of allethrin were as follows: cinerin I 0.0020, pyrethrin I 0.0010, cinerin II 0.0050, pyrethrin II 0.0026, allethrin 0.025 percent (w/v).--Ward (117). Rothamsted Experimental Station (90).

This beetle was used in testing esters of *d-trans* chrysanthemumic acid with the *d* and *l* forms of allethrolone. The ester from the *d* form of the alcohol proved to be four or five times as toxic as that from the *l* form. These esters act independently without synergism or mutual depression of activity.--Rothamsted Experimental Station (89).

Coleoptera: Curculionidae

Sitophilus oryza (L.), rice weevil

In experiments conducted in Alabama sprays containing piperonyl butoxide did not prevent rice weevil damage to shucked ear corn and corn in the shuck.--Eden (20).

Coleoptera: Dermestidae

Trogoderma granarium Everts, khapra beetle

Practically no kill was obtained when larvae were exposed for 2 hours to a deposit of 1,000 micrograms of allethrin per square centimeter.--Lindgren *et al.* (62)

Coleoptera: Bruchidae

Callosobruchus chinensis (L.), adzuki bean weevil

When polyoxyethylene nonylphenol was added to a 0.02-percent allethrin solution, the mortality of adults of these weevils decreased with increase in concentration of this wetting agent.--Hirota and Takeuchi (45).

Coleoptera: Tenebrionidae

Tenebrio molitor L., yellow mealworm

T. obscurus F., dark mealworm

An emulsion containing 0.5 percent of allethrin or pyrethrins, alone or with a synergist, is suitable for the treatment of wooden floors or walls of empty granaries or warehouses to prevent mealworm infestations. From 1 to 2 gallons per 1,000 square feet is recommended, depending on the condition of the woodwork and the amount of fluid required to saturate it.--Stored Product Insects Division, BEPQ (103, 104); Dove (17); Walkden *et al.* (116).

The toxicity to *Tenebrio molitor* adults of crystalline alpha-dl-isomer of allethrin compared to that of the noncrystalline part was found to be in the ratio 11:95.--Rothamsted Experimental Station (89).

Lepidoptera: Hyponomeutidae

Plutella maculipennis (Curt.), diamondback moth

A pyrophyllite dust containing 0.23 percent of allethrin was moderately effective.--Dills and Odland (16).

Lepidoptera: Phalaenidae

Diataraxia oleracea (L.)

Lower concentrations of allethrin were required to give a 50-percent kill in all ages of eggs at 57° F. than were required to give the same kill at 75°.--Salkeld and Potter (91).

Heliothis armigera (Hbn.), corn earworm

A 0.5-percent allethrin dust was ineffective as a repellent for the corn earworm in field tests in South Carolina.--Chamberlain (13).

Trichoplusia ni (Hbn.), cabbage looper.

Same as for *Plutella maculipennis*.--Dills and Odland (16).

Lepidoptera: Pieridae

Pieris rapae (L.), imported cabbageworm

Same as for *Plutella maculipennis*.--Dills and Odland (16).

Lepidoptera: Pyraustidae

Diaphania nitidalis (Stoll), pickleworm

When applied to the insects in laboratory cage tests a 0.5-percent allethrin dust proved toxic to third instars, but it was less effective against last instars, even when used at a heavy dosage. A 2-percent allethrin dust showed only moderate toxicity to last-instar pickleworms. The addition of piperonyl butoxide, piperonyl cyclonene, an activated nicotine, or compound 469 did not appreciably increase the toxicity of a 0.5-percent allethrin dust.--Reid and Cuthbert (87).

Pyrausta nubilalis (Hbn.), European corn borer

At Ankeny, Iowa, an emulsion of allethrin, 1 pound per 100 gallons of water, gave a 77-percent reduction of borers, and 25-percent wettable powders at the same dosage caused reductions of 84 and 90 percent. Sprays were applied to the whorl of the corn plants at approximately 120 gallons per acre.--Questel and Brindley (85).

Lepidoptera: Phycitidae

Ephestia kuhniella Zell., Mediterranean flour moth

In laboratory spraying experiments allethrin was more toxic to 5-day-old eggs than those 1 day old.--Salkeld and Potter (91).

Diptera: Culicidae

Aedes aegypti (L.), yellow-fever mosquito

In laboratory tests allethrin was compared with pyrethrins in the form of colloidal water solutions and oil emulsions. The LD-50 for larvae was 0.033 p.p.m. for pyrethrins and 0.083 p.p.m. for allethrin. Synergists did not materially increase the toxicity of allethrin.--Ginsburg (34).

Laboratory experiments showed allethrin to be 25 to 40 percent as toxic as the natural pyrethrins to larvae and pupae.--Ginsburg (35).

Furethrin, allethrin, and pyrethrins sprays were compared in a Peet-Grady chamber at a dosage of 13.9 ml. per 1,000 cubic feet. The furethrin and allethrin sprays were used at concentrations of 0.264 and 0.528 mg., and the pyrethrins at 0.033 and 0.066 mg. per milliliter. Similar mortalities were obtained in all cases, indicating that the synthetics were about one-eighth as effective as the pyrethrins.--Fales et al. (23).

Aedes dorsalis (Meig.) and flavescens (Mueller)

Allethrin injected into calves at 100 mg./kg. was ineffective as a chemotherapeutic agent for control of these mosquitoes.--Lindquist et al. (63).

Aedes cinereus Meig., communis (Deg.), excrucians (Walker), fitchii (Felt and Young), hexadontus Dyar

In tests for the control of these snow-water mosquitoes in the Cascade Mountain area of Oregon, space sprays containing 0.2 or 0.4 percent of pyrethrins or allethrin gave satisfactory control in limited areas during the evening migration period.--Hoffman and Lindquist (46).

Aedes nigromaculis (Lud.)

In laboratory tests against DDT-resistant adult mosquitoes 2 to 7 days old, the mortality 24 hours after 1-minute exposure to aerosols containing 10.5 mg. of toxicant per 1,000 cubic feet was 70 percent for pyrethrins and 40 percent for allethrins.--Gjullin (36).

Anopheles quadrimaculatus Say, common malaria mosquito

The toxicity (LD-50) of allethrin to 4-day-old adults was 0.0029 microgram for males and 0.008 for females. Allethrin was the most toxic material tested, 6.9 times as toxic as p,p'-DDT to male mosquitoes and 8.3 times as toxic to females.--Lukvik (65).

Culex quinquefasciatus Say (= fatigans Wied.)

Laboratory tests were made against 2-day-old adult mosquitoes using 5 ml. per 1,000 cubic feet and an exposure time of 20 minutes. Allethrin at 0.1 percent plus 0.5 percent of n-propyl isome was about equal to 0.1 percent of pyrethrins in 20-minute knockdown and 24-hour kill. Allethrin at 20 mg. plus n-propyl isome at 200 mg. per square foot had little residual action.--Rajindar Pal and Krishnamurthy (86).

Culex pipiens var. pallens Coq.

Against larvae of this species crystalline pyrethroresine and its decomposition product exhibited no toxicity and no synergistic action when mixed with pyrethrins or allethrin.--Tamura and Matsubara (105).

In laboratory tests at Fresno, Calif., against DDT-resistant adult mosquitoes 2 to 14 days old, mortality 24 hours after exposure to aerosols containing 10.5 mg. of toxicant per 1,000 cubic feet was as

follows: After 2 minutes, pyrethrins 53 and allethrin 20 percent; after 3 minutes, pyrethrins 81 and allethrin 52 percent. With residual sprays against female mosquitoes the mortality 24 hours after a 1-hour exposure to a residue of 3 mg. per square foot was 67 percent for pyrethrins and 74 for allethrin.--Gjullin (36).

Unidentified mosquitoes

Campers and camp and resort organizations can obtain relief from the mosquito nuisance with a minimum of cost and effort by spraying to kill adult mosquitoes. For a 2-hour period in the early evening, when they are continuously flying, a quick-killing space spray containing pyrethrum or allethrin will give temporary protection by killing mosquitoes in flight.--U.S. Bureau of Entomology and Plant Quarantine (110).

An aerosol formula recommended for killing adult mosquitoes contains 2 percent of DDT, 0.6 percent of allethrin, 5 percent of alkylated naphthalene, 7.4 percent of deodorized kerosene, 42.5 percent of Freon-11, and 42.5 percent of Freon-12.--Stage *et al.* (98)

Diptera: Muscidae

Musca domestica L., house fly

In tests in California against normal and DDT-resistant house flies, allethrin was more than three times as toxic as pyrethrins.--March (66).

In extensive tests in dairy barns in Florida in 1950, space sprays of allethrin gave poor results. This was attributed chiefly to the high resistance of the flies.--Wilson *et al.* (120).

In tests by the turntable and Peet-Grady methods aerosols containing 0.1 percent of allethrin plus MGK-264, Lethane 384, and DDT were as effective 2 years after being prepared as when first made up.--Moore *et al.* (75).

When tested by the Peet-Grady method, allethrin at 1.5 mg./ml. killed 50 percent in 24 hours and gave a complete knockdown.--Lockard and Fish (64).

Technical allethrin was about 1.46 times as toxic as *dl*-*trans*-allethrin to house flies.--Nagasawa (78).

In laboratory tests and tests in food establishments in California, residual applications of allethrin were not effective in controlling the flight distance of house flies.--Sampson (92).

In tests using a measured drop technique, pyrethrins proved twice as toxic as allethrin to the house fly.--Nash (81).

In New Zealand allethrin at 0.1 and 0.2 percent in kerosene, tested by the modified Peet-Grady method, was about as effective in both knockdown and mortality as pyrethrins at the same concentrations.--Harrison (41).

When their relative toxicity to susceptible and DDT-resistant female house flies was evaluated by the topical application method, allethrin was found to be equally as toxic as pyrethrins to both strains.--Mitlin and Babers (70).

Siphona irritans (L.), horn fly

Stomoxys calcitrans (L.), stable fly

Emulsion concentrates containing 10 parts of piperonyl butoxide to 1 part of pyrethrins diluted with up to 19 parts of water gave excellent protection to dairy cows against the horn fly for 5 to 12 days, and against the stable fly for 1 to 2 days, and partial protection against both species for a few additional days. About twice as much allethrin was needed to maintain comparable protection.--Moore *et al.* (74).

Diptera: Sarcophagidae

Sarcophaga peregrina (R. D.)

Pyrethrins and allethrin as 1-percent emulsions were only slightly effective against third-instar larvae, and allethrin had the lower effectiveness.--Toyama and Takeshi (106)

Diptera: Tabanidae

Chrysops bishoppi Bren. and *discalis* Will, *Tabanus productus* Hine, *punctifer* O. S., and *sonomensis* O. S.

Allethrin at 100 mg./kg. was ineffective when injected into calves for control of these tabanids.--Lindquist *et al.* (63).

Tabanus atratus F., black horse fly

Same as for *Stomoxys calcitrans*.--Moore *et al.* (74).

Tabanus sulcifrons Macq., horse fly

A spray containing 1 percent of allethrin plus 10 percent of MGK 264 was found to have a repellency of 81.3 percent. A similar formulation containing pyrethrins had a repellency of 92.8 percent. Increasing the

allethrin content to 2 percent raised the repellency to 92.2 percent. A formulation containing 11.8 percent of dimethyl carbate and 2 percent of allethrin had a repellency of 92.4 percent; a formulation containing the same amount of dimethyl carbate and 1.18 percent of pyrethrins had a repellency of 90.4 percent.--Bruce and Decker (8).

Diptera: Tephritidae

Dacus cucurbitae Coq., melon fly

Dacus dorsalis Hendel, oriental fruit fly

Ceratitis capitata (Wied.), Mediterranean fruit fly

In laboratory tests in Hawaii with emulsions in a settling tower, 200 seconds' exposure was required to kill all the fruit flies with allethrin.--Ebeling (18).

Hymenoptera: Apidae

Apis mellifera L., honey bee

In laboratory tests 0.26-percent allethrin dust at a dosage of 400 mg. killed only 9 percent of honey bees in 72 hours. Pyrethrins at the same dosage killed 13 percent.--Atkins and Anderson (6).

Hymenoptera: Formicidae

Iridomyrmex humilis Mayr, Argentine ant

Monomorium minimum Buckl., little black ant.

M. pharaonis (L.), Pharaoh ant

A kerosene spray of allethrin 0.1 percent plus piperonyl butoxide 1 percent gave only brief protection against Argentine ants. Three applications failed to give protection for more than 6 weeks. In tests against the little black ants, pyrethrum and allethrin failed to give 1 week of protection indoors, and repeated applications failed to control these ants for the season. Allethrin gave little or no control of the Pharaoh ant.--Laudani and Vanderford (58).

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